

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Cracking Gas-Oils

We, ESSO RESEARCH AND ENGINEERING COMPANY, formerly known as Standard Oil Development Company, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the catalytic conversion of gas oils to lower boiling components.

In a conventional catalytic conversion process of the type indicated, a gas oil is contacted with a bed of catalytic material in a reactor to convert the gas oil to lower boiling components. For this purpose a number of types of catalyst beds have been employed such as fixed beds, moving beds and fluidized beds, all of which are well known in the petroleum industry. During the contacting of the gas oil with the catalyst, in any of the aforementioned types of catalyst beds, a carbonaceous or coke-like deposit is laid down on the catalyst. This carbonaceous deposit reduces the effectiveness of the catalyst to convert the gas oil to lower boiling components and it is therefore necessary to remove this coke-like deposit from the catalyst, or in other words, to regenerate the catalyst so that the catalyst may be used for further catalytic cracking. This is accomplished by separating the coke-fouled or spent catalyst from the hydrocarbons and burning off the coke-like deposit with an oxygen-containing gas. Although the catalyst prior to regeneration is normally called "spent" catalyst, its catalytic activity actually is only partially spent. In general, though, a major portion of its catalytic activity has been lost.

By changing reaction conditions, such as temperature, space velocity, and residence time, the conversion of gas oil to gasoline may be increased in a catalytic cracking process. However, in general, as the conversion of gas oil to gasoline is increased, the amount of coke formed and laid down on the catalyst also increases. Although it is desirable to maximize

the amount of gas oil converted to gasoline, the extent of this conversion is thus limited by the amount of carbonaceous or coke-like deposits laid down on the catalyst and the facilities provided for burning off these carbonaceous deposits. Therefore, there is normally an economic balance between the conversion of gas oil to gasoline and the investment required for regeneration facilities. As regeneration facilities represent a substantial portion of the investment for a catalytic cracking system, the conversion of gas oil to gasoline in a given catalytic cracking system is therefore normally limited to the capacity of the regeneration facilities which were originally economically justified. The above problems are particularly severe in the case of certain gas oils containing a large proportion of aromatics or are high in nitrogen and which are such as to produce a substantially higher ratio of coke to gasoline than will paraffinic or naphthenic gas oils.

The principal object of the present invention is to effect a high conversion of gas oil to gasoline while at the same time minimizing the amount of coke formed on the catalyst, and in accordance with the invention this is achieved by a process which comprises maintaining the gas oil in contact with freshly regenerated catalyst in a conversion zone at from 850—1000° F. until there is produced a vaporous hydrocarbon product containing a substantial amount of hydrocarbon components boiling below 430° F. together with coke, not more than 5% by weight of the gas oil being converted to coke, passing the product substantially free of catalyst into a soaking zone where it is heated to a temperature in the range of about 850° to 1150° F. to produce additional hydrocarbon components boiling below 430° F. but substantially no coke.

In a first form, of the present invention, a gas oil, substantially all of which boils above about 430° F. is contacted with a cracking catalyst at a temperature of about 850—1000° F. and preferably at a temperature of about 900—950° F. so that between about 30—50% by volume of the gas oil is converted to gasoline (i.e. hydrocarbon material boiling below

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Price 25s

430° F. including C₈s but not including C₉s or lighter material), other components boiling below about 430° F. (i.e. hydrocarbon material including the C₉s) and coke so that not more than about 5% by weight of the gas oil is converted to coke. The resultant vaporous lower boiling hydrocarbon products are then separated from the resultant spent catalyst so that the catalyst concentration in the separated vaporous hydrocarbon products does not exceed more than about 0.1 lbs. of catalyst/cubic foot. The substantially catalyst free vapors are then preferably heated to a temperature of about 1050—1150° F. and preferably to a temperature of about 1075—1125° F. and are maintained or soaked in that temperature range for about 0.5—10 seconds so that about an additional 5—20% by volume of the vaporous hydrocarbons are converted to gasoline and other components boiling below about 430° F. During this soaking step, substantially no coke is formed. Thereafter the hydrocarbon vapours are recovered and fractionated into a number of desired fractions including a gasoline fraction. Thus the initial contacting of the hydrocarbon gas oil with the catalyst results in the major portion of the conversion of the hydrocarbon gas oil to high-quality gasoline and the subsequent soaking step or predominantly thermal cracking step provides additional conversion with essentially no further coke formation. The present invention is applicable to hydrocarbon gas oils generally but is especially useful for high carbon-producing gas oils.

In a second form of the invention, instead of carrying the soaking step at a temperature of from about 1050 to 1150° F. as above described, such step may be conducted at a temperature between about 850—1050° F. and preferably at a temperature of about 900—1000° F., in which case the treatment time will be about 0.5—5 minutes to achieve the additional 5—20% by volume of the hydrocarbons conversion to gasoline and other components boiling below about 430° F. During this alternative soaking procedure also, substantially no coke is formed; however, because a certain amount of diolefins is produced during this soaking step, the resultant hydrocarbons are then further contacted in an aftertreating step with additional catalyst, which is preferably the partially spent catalyst from the initial catalytic cracking step, so as to convert most of the diolefins to saturated hydrocarbon products.

The initial contacting of the hydrocarbon gas oil with catalyst results in the major portion of the conversion of the hydrocarbon gas oil to high quality gasoline. The soaking step, or predominantly thermal cracking step, provides additional conversion with essentially no further coke formation but a certain amount of diolefins are formed. About 2—5% of the total hydrocarbons from the soaking

zone are diolefins. The elimination of these diolefins in the catalytic aftertreating step, which also produces a small amount of coke, substantially improves the stability of the final hydrocarbon products, including both gasoline and middle distillates, so that they are stable as to color and also will not oxidize to form undesirable gums and peroxides. The catalytic after-treating step also improves the octane number of the gasoline fraction of the hydrocarbon products from the present invention, and also effects a minor amount of additional conversion. Using the three steps, namely, initial catalytic cracking, soaking and catalytic aftertreating produces the overall desirable results of a high ratio of yield of gasoline to yield of coke in addition to stable gasoline and middle distillate products.

As an example of the second form of the invention, a catalytic cycle stock containing about 40 weight per cent aromatic rings will produce 6% by weight carbon at 40% conversion, 10% by weight at 50% conversion and about 16% by weight at 60% conversion in a conventional catalytic cracking process. From an economic standpoint, it would be very desirable to crack the cycle stock to a conversion of 50—55%, for example, except for the high coke yield which would require very large regeneration facilities. Such a requirement is alleviated by modified form of the invention as the cycle stock would be processed to only about 35% conversion in the initial catalytic cracking step of the modified form of the invention. The hydrocarbon products from this initial catalytic cracking step would then be maintained at a temperature of about 950° F. for about 1 minute. At the end of this period a total conversion in the order of 50% would be achieved. The coke formation as a result would be only about 5% by weight in the present invention, as compared to 10—13% by weight in a conventional catalytic cracking process. In another example where cracking of a high nitrogen content gas oil will produce 6% by weight of coke at 45% conversion and 10% by weight of coke at 55% conversion in a conventional catalytic cracking process, the gas oil would be converted according to the present process to 35—40% conversion in the initial catalytic cracking step and the resultant hydrocarbon products soaked for about 1 minute at about 950° F. to produce a final conversion of 50—55% with a coke yield of less than 5% by weight. In this example, and in the preceding example, the catalytic aftertreating step will produce a minor increase in coke and conversion.

The process of the present invention will be readily understood by reference to the accompanying drawings in which:—

Figure 1 is a diagrammatic view of one form of apparatus adapted to carry out the process of the first form of the invention;

Figure 2 is a diagrammatic view of another form of apparatus adapted to carry out the process of the first form of the invention; and

Figure 3 is a diagrammatic view of one form of apparatus adapted to carry out the second form of the invention with parts broken away to facilitate the disclosure.

Referring now to Figure 1, reference character 10 designates a vessel or reactor adapted to carry out a catalytic conversion of a gas oil with a finely divided fluidized catalyst. In this specific embodiment of the present invention, hot freshly regenerated catalyst is introduced into the bottom of reactor 10 through inlet conduit 11 and its rate of introduction thereto is controlled by means of valve 12 in conduit 11. The catalyst employed may be a natural catalytic substance, such as acid-treated clay, or a synthetic catalytic substance such as silica-alumina and silica-magnesia. In general the finely divided catalyst particles have a size of less than about 250 microns in average diameter and normally the particles will have a size range such that substantially all of them are between about 20—100 microns in average diameter. The catalyst flowing through conduit 11 will normally be obtained from a regenerator (not shown) wherein carbonaceous deposits are burned off the spent catalyst produced in the process as will hereinafter be described in detail. Thus in the specific embodiment of the present invention as shown in Fig. 1 the finely divided catalyst will be continuously passed between reactor 10 and the regenerator which may be any conventional regenerator adapted to regenerate a finely divided catalyst.

Prior to the introduction of the finely divided catalyst into the bottom of reactor 10, it is combined with a gas oil introduced into conduit 11 through conduit 13 at a rate regulated by means of valve 14 in conduit 13. The gas oil will generally have a boiling range between about 400—1050° F. Normally the gas oil introduced through conduit 13 will have been preheated to a temperature which may be as high as about 700° F. by indirect heat exchange with high temperature product streams or by a preheat furnace (not shown). The amount of preheat required will depend upon a number of factors such as the temperature of the regenerated catalyst in conduit 11 which may be about 1000—1150° F., the catalyst-to-oil feed ratio to vessel 10 which may be from about 5—15 by weight, and the reaction temperature desired in vessel 10.

The catalyst-oil mixture is then introduced into the bottom of reactor 10 at a rate such that the superficial velocity of the oil vapors rising upwardly therein will be about 0.5—5 ft./sec. and preferably about 1—3 ft./sec. At these vapor velocities the finely divided catalyst will form a dense fluidized bed 15 in the lower portion of vessel 10 with the bed having a density of about 30—50 lbs./cu.ft. The reac-

tion temperature in vessel 10 will be maintained at about 850—1000° F. and preferably at about 900—950° F. and the pressure in reactor 10 will normally be maintained at about 0—50 lbs./sq.in. gauge (psig). As previously stated, the finely divided catalyst in reactor 10 will be generally maintained as dense bed 15 in the lower part of reactor 10 and this dense bed will have a relatively well-defined upper level L which is maintained thereat by continuously withdrawing catalyst from dense bed 15 by means of outlet conduit 20 which extends through vessel 10 up into dense bed 15 at a position slightly below upper level L. The rate of withdrawal of catalyst from dense bed 15 through conduit 20 is regulated by means of valve 21 in conduit 20. The catalyst hold-up in reactor 10 should be sufficient to provide a space velocity of about 1—5 lbs. of hydrocarbon oil/hour/lb. of catalyst hold up in reactor 10. The catalyst removed from dense bed 15 through conduit 20 is passed to the previously mentioned regenerator (not shown) associated with reactor 10 wherein carbonaceous deposits are burned off the spent catalyst with air, after which the resultant regenerated catalyst is passed back to reactor 10 through conduit 11.

Thus in the specific embodiment of the present invention shown in Fig. 1, the hydrocarbon vapors are passed upwardly in reactor 10 through dense bed 15 wherein they are converted to lower boiling products and coke which is deposited on the finely divided catalyst to produce spent catalyst. The reaction conditions in reactor 10 are adjusted such that about 30—50% of the hydrocarbon gas oil introduced into the bottom of reactor 10 is converted to products boiling below about 430° F. and coke, and so that no more than about 5% by weight of the hydrocarbon gas oil is converted to coke. After flowing through dense bed 15, the converted hydrocarbon vapors enter dilute or disperse phase 22 located in reactor 10 above upper level L of dense bed 15. Disperse phase 22 contains a small amount of catalyst which is entrained with the vapors rising from dense bed 15. The rising hydrocarbon vapors in disperse phase 22 pass upwardly out of reactor 10 through outlet conduit 23. These vapors are essentially free of entrained catalyst and contain no more than about 0.1 lbs. of catalyst/cu. ft. of hydrocarbon vapors, and normally contain only about 0.002—0.05 lb. of catalyst/cu. ft. of vapors.

The hydrocarbon vapors passing upwardly through conduit 23 from reactor 10 are introduced into heat exchanger 30 wherein they flow through the interior of tubular heating coil 31. In heat exchanger 30, the hydrocarbon product vapors are heated to a temperature of about 1050—1150° F. and preferably to a temperature of about 1075—1125° F. It is to be clearly understood that all of the vaporous hydrocarbon products formed in reactor 10 are

heated to this particular temperature, namely 50—300° F. above the temperature existing in reactor 10. Heat exchanger 30 may, for example, comprise a furnace into which is introduced a gas or oil fuel through conduit 32 containing valve 33 and an oxygen-containing gas such as air through conduit 34 containing valve 35. The rates of introduction of oil and air through conduits 32 and 34, respectively, are controlled by means of valves 33 and 35, respectively, to produce a combustible mixture which is burned in the interior of heat exchanger or furnace 30. The gaseous products of combustion from heat exchanger 30 are removed therefrom through conduit 37.

Instead of utilizing heat exchanger 30 as a furnace, it may be practical to introduce the hot flue gas from the regenerator associated with reactor 10 into the interior of heat exchanger 30 through conduits 32 and 34. Thus if the temperature of the regenerator flue gas is about 1100° F. or above, it may be employed in heat exchanger 30 to heat the product vapors passing through coil 31. In this case, conduit 37 may be employed to continuously remove the cooled regenerator flue gas from exchanger 30. The gases exiting from heat exchanger 30 through conduit 37 may be vented directly to the atmosphere or may be passed through other heat exchangers to recover a major portion of their sensible heat. For example, the hot gases passing from heat exchanger 30 through conduit 37 may be employed to preheat the fresh hydrocarbon gas oil which is introduced to the system of the present invention through conduit 13.

The length and diameter of coil 31 are selected so that the vaporous hydrocarbon products which are introduced thereto from conduit 23 will be heated to a temperature of about 1050—1150° F., and preferably to a temperature of about 1075—1125° F., because it will be necessary to maintain the heated vapors in this temperature range for about 0.5—10 seconds prior to their being fractionated into desired fractions as will hereinafter be described in detail. The particular length and diameter of coil 31 required will be dependent upon the hydrocarbon vapor flow rate, the temperature of the heating medium in heat exchanger 30, and the heat exchange coefficients involved. The temperature to which the hydrocarbon vapors are heated in coil 31 and the residence time of the vapors in the temperature range of 1050—1150° F. prior to fractionation should be selected such that an additional 5—20% of the hydrocarbon vapors are converted to products boiling below about 430° F. The required residence time of the vapors in the specified temperature range will depend of course upon the temperature involved; thus the higher the temperature, the shorter the residence time, and *vice versa*. Thus flexibility of conversion may be readily attained by regulating the extent of heating in

coil 31. The additional amount of converted hydrocarbons will comprise mainly additional gasoline and dry gas (C_3 and lighter gases). In addition to these products a very small amount of the vaporous hydrocarbons introduced into coil 31 will be converted to coke. Normally this amount of coke will not exceed more than about 0.5% by weight of the original hydrocarbon gas oil fed to reactor 10 through conduit 13.

The heated hydrocarbon vapors are removed from coil 31 by means of conduit 40 which communicates at its other end with the interior of cyclone separator 41. The heated hydrocarbon vapors which are being thermally cracked are introduced tangentially into housing 42 of cyclone separator 41 through inlet 43. In housing 42 the vapors are swirled around, so that the small amount of entrained catalyst is thrown against the inner wall of housing 42 by centrifugal force and is separated from the bulk of the hydrocarbon vapors. The catalyst falls downwardly along the inner wall of housing 42 and flows downwardly from housing 42 through dipleg 45 which communicates at its lower end with dense bed 15 in reactor 10. Thus the entrained finely divided catalyst is separated from the hydrocarbon vapors in cyclone separator 41 and is returned to the system by means of dipleg 45 which extends at its lower end beneath upper level L of dense bed 15. The separated hydrocarbon vapors are removed from cyclone separator 41 through outlet conduit 44 which is arranged centrally in housing 42 and which communicates with the upper portion thereof. It will be understood that the positions of cyclone separator 41 and heat exchanger 30 may be interchanged so that the hydrocarbon vapors from reactor 10 would be passed through cyclone separator 41 first and then through heat exchanger 30 after which the resultant heated vapors would be passed into conduit 44. In this case cyclone separator 41 could be arranged within the upper portion of reactor 10, if desired.

The hot hydrocarbon vapors passing through conduit 44 are introduced into the lower portion of fractionator 50 wherein the hydrocarbon products are partially cooled by refluxing and are separated into at least two fractions. It will be understood that the residence time of 0.5—10 seconds required for soaking the heated hydrocarbon vapors in the temperature range of 1050—1150° F. extends from coil 31 to fractionator 50. Cyclone separator 41 and conduits 40 and 44 are preferably insulated in order to maintain the hydrocarbons at this soaking temperature. In this specific embodiment of the present invention, gasoline and other components boiling below about 430° F. are removed overhead from fractionator 50 through conduit 51 and components boiling above about 430° F. are removed as a bottoms fraction through conduit 52. It will be understood however that the hydrocarbon products

may be fractionated into more product streams if desired by providing fractionator 50 with sidestream drawoffs (not shown). Fractionator 50 may be any conventional fractionating means for separating hydrocarbons and thus may be provided with bubble-cap trays or jet trays to increase the fractionating efficiency. If desired, a cooling means may be installed in the apparatus shown in Fig. 1 in order to partially cool the vapors from heat exchanger 30 before the vapors are introduced into cyclone separator 41. Thus for example the vapors could be cooled to about 850—900° F. prior to their introduction into cyclone separator 41. In this event, however, the vapors should be maintained in exchanger 30 at a temperature of about 1050—1150° F. for 0.5—10 seconds so that the additional 5—20% conversion will be obtained. This may be readily accomplished by increasing the capacity of coil 31 so that the residence time of the vapors in heater 30 is increased sufficiently to accomplish the desired conversion. Thus it will readily be seen that there are many forms of apparatus which may be employed to carry out the method of the present invention.

Referring now to Fig. 2, reference character 100 designates an elongated vessel which is adapted to carry out a hydrocarbon conversion reaction in the presence of a finely divided catalyst and which will be termed transfer line reactor 100. A finely divided fluidized catalyst is introduced into the bottom of transfer line reactor 100 through conduit 101 containing valve 102. The finely divided catalyst in this specific embodiment of the present invention has a size of less than about 250 microns in average diameter and generally all of the finely divided catalyst will have a size range of about 20—100 microns. The finely divided catalyst passing through conduit 101 is normally a hot freshly regenerated catalyst obtained from a regenerator (not shown) wherein carbonaceous deposits have been burned off of spent catalyst which is produced in the process of the present invention as will be hereinafter described in detail.

A hydrocarbon gas oil having a boiling range between 400—1050° F. is introduced into conduit 101 through conduit 103 containing valve 104 for admixture therein with the finely divided catalyst. This hydrocarbon gas oil may be preheated to a temperature as high as about 700° F. by means of heat exchangers (not shown) or by a preheat furnace (not shown). The relative amounts of catalyst and hydrocarbon gas oil introduced into the bottom of reactor 100 are regulated by means of valves 102 and 104 in conduits 101 and 103, respectively. The rate of introduction of the gas oil-catalyst mixture in transfer line reactor 100 is adjusted so that the upward superficial velocity of the rising hydrocarbon vapors therein will be about 6—15 ft./sec. and so that the catalyst concentration in transfer line reactor 100 will

be about 10—20 lbs./cu.ft. Under these conditions, the hydrocarbon vapors and catalyst will flow upwardly in transfer line reactor 100 substantially concurrently such that no dense bed of finely divided catalyst having a well-defined upper level as in the specific embodiment shown in Fig. 1 will be formed in the bottom of reactor 100. In flowing upwardly through transfer line reactor 100, the vaporous hydrocarbon gas oil at a temperature of about 75 850—1000° F. is converted to about 30—50% by volume of products boiling below about 530° F. and coke which is deposited on the finely divided catalyst. The amount of coke formed should not exceed more than about 5% 80 by weight of the original hydrocarbon gas oil.

The resultant suspension of lower boiling vaporous hydrocarbon products and spent catalyst are withdrawn from the top of transfer line reactor 100 through conduit 110 which 85 communicates at its other end with cyclone separator 111. The vaporous hydrocarbon products and catalyst are introduced tangentially into housing 112 of cyclone separator 111 through inlet 113. The catalyst-oil suspension 90 is swirled around in housing 112 to effect a rapid separation of the finely divided catalyst from the hydrocarbon vapors which are removed from the upper part of housing 112 through centrally located outlet pipe 114. The 95 separated catalyst particles flow downwardly out of housing 112 through conduit 115 wherefrom the separated finely divided catalyst is passed to a regenerator (not shown) so as to burn off the carbonaceous deposits from the spent catalyst. Subsequently this regenerated catalyst is reintroduced into transfer line reactor 100 from the regenerator through conduit 101 for contact with additional hydrocarbon gas oil. 100 105

The vaporous hydrocarbon products which are substantially freed of the finely divided catalyst in cyclone separator 111 are passed therefrom through conduit 114 into heat exchanger 120 wherein they flow through the interior of tubular heating and soaking coil 121. Heat exchanger 120 may, for example, comprise a furnace wherein a liquid or gaseous fuel is introduced to the interior thereof through line 122 containing valve 123 and wherein an 115 oxygen-containing gas such as air is introduced to the interior thereof through line 124 containing valve 125. Valves 123 and 125 in lines 122 and 124, respectively, are regulated so as to produce in the interior of heat exchanger 120 a combustible mixture which is burned to effect the heating desired in this invention. In this case the products of combustion are removed from the interior of heat exchanger 120 through outlet pipe 126. The gaseous products of combustion exiting from heat exchanger 120 through outlet line 126 may be vented directly to the atmosphere or may be first passed through other heat exchange equipment (not shown) to recover the major portion 130

of their sensible heat. Alternatively heat exchanger 120 may employ hot flue gases having a temperature of about 1050—1150° F. which are produced in the regenerator which is associated with transfer line reactor 100. In this case, the hot flue gases from the regenerator would be introduced through line 123 and/or line 124 and would be removed from the interior of heat exchanger 120 through outlet line 126.

The diameter and length of coil 121 are selected so that the vaporous hydrocarbon products passing through coil 121 are heated therein to a temperature of about 1050—1150° F. and preferably to a temperature of about 1075—1125° F. The dimensions of coil 121 which are required will depend, for example, upon the heat transfer coefficients involved and the temperature of the heating medium. Also it is necessary that the resultant heated vapors be maintained in this temperature range for about 0.5—10 seconds prior to being fractionated into desired fractions as will hereinafter be described in detail so that an additional 5—20% of the original hydrocarbon gas oil is converted to products boiling below 430° F. and a very small amount of coke which will not exceed more than about 0.5% by weight of the original hydrocarbon gas oil. It is to be clearly understood that all of the vaporous hydrocarbon products formed in reactor 100 are heated to this particular temperature, namely 50—300° F. above the temperature existing in reactor 100. The particular temperature to which the hydrocarbon vapors are heated in heat exchanger 120 and their residence time in the temperature range of about 1050—1150° F. prior to fractionation will of course be dependent upon the thermal cracking properties of the particular hydrocarbon gas oil introduced into the system.

The heated vaporous hydrocarbons which are being thermally cracked are removed from coil 121 of heat exchanger 120 by means of conduit 130 which communicates at its other end with fractionator 131 wherein the hydrocarbon products are partially cooled by refluxing and are separated into at least two product streams. In this embodiment of the invention the converted hydrocarbons are separated into a fraction boiling below about 430° F. which is taken off overhead through conduit 132 and a bottoms fraction which is withdrawn through conduit 133. However, it will be understood that additional product streams may be taken off by providing fractionator 131 with side-stream drawoffs (not shown). Fractionator 131, which is of conventional design, may be provided with bubble cap trays or jet trays, in order to improve its fractionating efficiency. If desired, the thermally cracked vapors from heat exchanger 120 may be cooled or quenched below an active cracking temperature before they are introduced into fractionator 131 by passing the vapors through heat exchangers

or quenching towers (not shown). However, it is essential that the vapors prior to this cooling or quenching step be maintained in the temperature range of about 1050—1150° F. for 0.5—10 seconds so that the desired additional conversion is obtained.

It is to be understood that the present invention is not limited solely to fluidized solids systems such as the dense fluid bed type shown in Fig. 1 and the transfer line reactor type shown in Fig. 2. Thus, more specifically the process of the present invention is also ideally suited for utilization in a system in which the catalyst is maintained either as a fixed bed or as a moving bed. In either of these two latter types of systems, the present process could be accomplished by passing the hydrocarbon gas oil vapors through the catalyst bed under cracking conditions of temperature (850—1000° F.) and pressure (0.50 psig) such that about 30—50% of the hydrocarbon gas oil would be converted to products boiling below 430° F. and a small amount of coke not exceeding more than about 5% by weight of the original hydrocarbon gas oil.

The resultant vaporous reaction products from the catalytic cracking step would then be heated to about 1050—1150° F. and maintained in this temperature range for about 0.5—10 seconds to convert an additional 5—20% of the original hydrocarbon gas oil to products boiling below 430° F. and a small amount of coke not exceeding 0.5% by weight of the original hydrocarbon gas oil, after which the resultant further converted hydrocarbon vaporous products would be separated into desired product fractions. When the method of the first form of the present invention is employed with a fixed catalyst bed or a moving catalyst bed, the present invention would be somewhat simplified in that there would be essentially no problem involved in the entrainment of catalyst in the vaporous hydrocarbon products as is encountered in the fluidized systems. However, the fluidized systems generally exhibit certain advantages over the fixed bed and moving bed types of system such as better utilization of heat from the regenerator, and easier control of process variables.

The following experiment was carried out and is set forth hereinafter in order to illustrate the advantages to be derived from the method of the first form of the invention as compared to the conventional catalytic cracking process. The experimental data was obtained from a 68 gram batch fluid catalytic cracking unit in which an Elk Basin heavy gas oil, which is a typical catalytic cracking feed stock, was catalytically cracked with a commercial silica-magnesia catalyst having a size range of about 44 to 147 microns. The Elk Basin heavy gas oil had a boiling range of about 400 to 1050° F. and a gravity of about 23° A.P.I. In general, the finely divided silica-magnesia catalyst was maintained during this experiment

in the bottom of the reactor of the catalytic cracking unit in the form of a dense fluidized bed. Above this dense fluidized bed there was a dilute phase or vapor space in which the concentration of catalyst was about 0.01 lb./cu.ft. This dilute phase was provided with an electrical heating means so that the temperature in the dilute phase could be maintained at a higher temperature than that existing in the dense bed. The vaporous hydrocarbon products were passed from the cracking unit through a water jacketed condenser and were collected in a receiver placed in a dry ice-oil bath. The condensed liquid hydrocarbon products were then cut in a small batch still to determine product yields.

In the first part of this experiment, the dense bed and the dilute phase were maintained

at the same temperature, namely, 925° F., and the Elk Basin gas oil was catalytically cracked under the conditions set forth in the table below. After the gasoline and carbon yields and conversion had been determined for these operating conditions, the operating conditions were changed so that in the second part of the experiment the dense bed was maintained at about 925° F. and the dilute phase or vapor space above the dense bed was maintained at 1100° F. by employing the previously mentioned heating means. Again the carbon and gasoline yields and conversion were determined for this second set of operating conditions. The following results were obtained for (1) the conventional catalytic cracking method and (2) the catalytic-thermal cracking method of the present invention:—

	Conventional catalytic cracking	Present invention combination catalytic-thermal
Catalyst dense bed temp., °F. - - - -	925	925
Vapor space temp., °F. (thermal) - - -	925	1100
Catalyst holding time, min. - - - -	2	2
Oil residence time in thermal zone, seconds		Approx. one sec.
Pressure, psig. (both zones) - - - -	0	0
Conversion, vol. % of feed - - - -	42.0	56.0
Carbon, wt. % of feed - - - -	4.1	4.5
Gasoline, wt. % of feed - - - -	31	39
Gasoline to carbon ratio - - - -	7.5	8.7
Carbon yield at comparable conversion levels (45%) - - - -	5.1	2.6

It will be noted from the experimental data that the per cent. conversion (per cent. of gas oil feed converted to products boiling below 430° F. and coke) obtained with the method of the present invention was substantially higher than that obtained with the conventional catalytic cracking method under comparable operating conditions. More specifically, the conversion obtained in accordance with the present invention was 14% higher than that of the conventional catalytic cracking method for comparable operating conditions. It will be further noted that this substantial increase in conversion was realized with only a slight increase in the amount of carbon produced. This increase in conversion was in part reflected by an 8% increase in the amount of gasoline produced. Thus, it will be seen that the gasoline-to-carbon ratio for the present invention was substantially higher than that of the conventional catalytic cracking process, namely 8.7 as compared to 7.5.

The advantage of the method of the present invention is even more emphatically brought out by the last set of figures presented in the above table wherein the carbon yields of the two methods were compared at the same conversion level, namely, 45%. Thus, it will be noted that at the same conversion level the method of the first form of the invention produces only about half as much carbon as does the conventional catalytic cracking method.

This substantial reduction in carbon is significant as this means that when employing the present process it is possible to employ a catalyst regenerator of only about half the capacity of that required in a conventional catalytic cracking process. Thus, it is apparent that the method will make possible substantial savings in the investment required for the regeneration portion of a catalytic cracking system. It is to be understood, however, that the improved results evidenced by the present invention may be realized either as an increased gasoline yield or as a decreased carbon yield, or as a combination of the two.

Fig. 3 illustrates one form of apparatus for carrying out the modification of the process of the present invention. This modification is illustrated with reference to the use of a finely divided catalyst which exhibits the properties of a fluid. The catalyst may be silica-alumina or silica-magnesia, having a particle size range such that substantially all of the catalyst is of a size of about 10—100 microns. It is to be understood, however, that the present process is applicable also to fixed bed and moving bed types of catalytic cracking systems. In Fig. 3 reference character 210 designates a reaction vessel for carrying out a portion of the modified process of the present invention, and reference character 211 designates a regenerator for burning off carbonaceous deposits on the fluidized catalyst in order to restore the catalytic

activity of the catalyst. Hydrocarbon gas oil and freshly regenerated catalyst are initially contacted in transfer line reactor 212 in which there is considerable turbulence. The freshly regenerated catalyst at a temperature of about 1000—1300° F. enters one end of reactor 212 by means of standpipe 213 leading from regenerator 211 and the hydrocarbon gas oil enters the same end of reactor 212 by means of conduit 214. Reactor 212, which in this specific embodiment of the present invention is inclined upwards at an angle, provides a contacting zone in which the initial conversion or cracking of the hydrocarbon gas oil to lower boiling components is effected.

The temperature in reactor 212 is maintained at about 850—1050° F. and preferably at about 900—1000° F. This is accomplished by preheating the hydrocarbon gas oil sufficiently so that when combined with the hot freshly regenerated catalyst leaving regenerator 211, the resultant oil and catalyst mixture is at such a temperature. The rate of flow of freshly regenerated catalyst from regenerator 211 through standpipe 213 is controlled by valve 216 and fluidization of the freshly regenerated catalyst in standpipe 213 is maintained by means of air or steam introduced through line 215. The length and diameter of reactor 212 is sufficient to convert about 30—50% of the hydrocarbon gas oil to gasoline, other low boiling components and coke without producing more than about 5% coke from the hydrocarbon gas oil. The space velocity of the vaporous hydrocarbon gas oil in reactor 212 is preferably between 10—100 w/w/hr. (weight of hydrocarbon feed/weight of catalyst/hr.) and the pressure in reactor 212 is preferably between 15—50 psig. In addition, the superficial velocity of the vaporous hydrocarbons in reactor 212 is preferably about 10 to 50 ft./sec. and the catalyst/oil ratio on a weight basis is preferably about 5—30.

The partially converted hydrocarbons and partially spent catalyst from reactor 212 are discharged into separating zone 217 of vessel 210. Reactor 212 connects tangentially with vessel 210 so as to impart a centrifugal action on the hydrocarbon vapors and partially spent catalyst. The catalyst particles are thus forced by the centrifugal effect to the wall of vessel 210 in separating zone 217. Annular plate 218, which defines the upper boundary of separating zone 217, is arranged horizontally on the inside of vessel 210 to aid in the separation of catalyst from the vaporous hydrocarbons. Not more than 20% of the cross-sectional area of vessel 210 is restricted by annular plate 218. The purpose of annular plate 218 is to prevent the layer of catalyst on the wall of vessel 210 from being swept upwardly by the rising hydrocarbon vapors. The superficial velocity of the hydrocarbon vapors is considerably lower in separating zone 217 than in reactor 212, being about 0.5 to 5 ft./sec. In separat-

ing zone 217, the partially converted vaporous hydrocarbons are thus separated from the partially spent catalyst, with the partially converted vaporous hydrocarbons flowing upward in vessel 210 through the opening in annular plate 218 and the partially spent catalyst flowing downward along the wall of vessel 210 in separation zone 217 due to the force of gravity. The further processing of these partially converted hydrocarbons will be presently discussed in detail.

The catalyst particles flowing downward from separating zone 217 enter a section of vessel 210 which is smaller in cross-section than separating zone 217 and which operates as stripping zone 219. The catalyst in stripping zone 219 is maintained as a dense turbulent fluidized bed. Steam or other suitable gas is introduced into the lower portion of stripping zone 219 by means of lines 220, so that substantially all of the hydrocarbons which are entrained with the downflowing catalyst are stripped from the partially spent catalyst. The steam and stripped hydrocarbon vapours from stripping zone 219 rise upward to separating zone 217. Baffles 221 are provided in stripping zone 219 to increase the effectiveness of the stripping operation. The major portion, namely, 50—95%, of the partially spent catalyst from stripping zone 219 flows downward through standpipe 222 into riser 223. Standpipe 222 is provided with valve 226 which regulates the flow of partially spent catalyst from vessel 210 into riser 223. Standpipe 222 is also provided with line 227 which introduces a fluidizing gas, such as steam, to maintain the partially spent catalyst in a fluid condition.

An oxygen-containing gas is introduced into the bottom end of riser 223 by means of conduit 224 and the mixture of the oxygen-containing gas and partially spent catalyst is passed through riser 223 into the lower part of regenerator 211. Grid 225 is employed at the discharge end of riser 223 to distribute the catalyst-gas mixture uniformly in regenerator 211. A small amount of the coke is burned off the catalyst in riser 223.

In regenerator 211 the remainder of the coke like deposits on the catalyst are burned off by the oxygen-containing gas. A dense turbulent fluid bed of catalyst particles is maintained in the lower portion of regenerator 211 at a temperature between about 1000—1300° F. A certain amount of the catalyst is carried upward in regenerator 211 from the dense fluid bed with the flue gases formed during the oxidation reaction. These entrained catalyst particles are removed by cyclone separator 245, arranged at the top of regenerator 211. The flue gases are withdrawn from regenerator 211 by means of conduit 246 and the catalyst particles separated from the flue gas are returned to the dense bed of regenerator 211 by means of dip leg 247.

The partially converted vaporous hydrocarbons after being separated from the partially spent catalyst in separating zone 217 of vessel 210 pass upward through the opening of annular plate 218 into soaking zone 229 in reactor vessel 210. Annular plate 218 in effect defines the boundary between separating zone 217 and soaking zone 229 in vessel 210. A temperature of about 850—1050° F. and preferably about 900—1000° F. is maintained in soaking zone 229. The average temperature in soaking zone 229 is approximately 15—25° F. lower than the average temperature in reactor 212. This is because the catalytic cracking step in reactor 212 and the thermal cracking step in soaking zone 229 are endothermic reactions which reduce the temperature of the hydrocarbon vapors. It is not necessary to add additional heat to the hydrocarbon vapors in soaking zone 229, although it is within the purview of the modified form of present invention to do so. At a temperature preferably of about 900—1000° F. the partially converted vaporous hydrocarbons are cracked in soaking zone 229 such that an additional 5—20% of the hydrocarbons are converted to gasoline and lower boiling components by maintaining the hydrocarbons in soaking zone 229 for about 0.5—5 minutes. A minor amount of the thermal cracking also occurs in separating zone 217 after the hydrocarbon vapors are separated from the catalyst and while these vapors are rising to soaking zone 229.

There is essentially no coke formation in soaking zone 229. A very small amount of coke is formed during the thermal cracking step in soaking zone 229 but this amount is insignificant as compared to the coke formed in reactor 212. Also, because a small amount of catalyst may be entrained with the hydrocarbon vapors passing to soaking zone 229 from separating zone 217 a small amount of coke will be formed on this entrained catalyst.

The vaporous hydrocarbon products from soaking zone 229 flow upward into a second contacting zone 230 in vessel 210 wherein the vaporous hydrocarbon products are contacted with partially spent catalyst. A small portion of partially spent catalyst, namely 5—50% of the partially spent catalyst from stripping zone 219, is withdrawn from standpipe 222 by means of standpipe 231. Standpipe 231 is provided with valve 232 which regulates the rate of flow of the partially spent catalyst particles in standpipe 231. Standpipe 231 is also provided with line 233 through which a fluidizing gas, such as steam, is introduced in order to maintain the partially spent catalyst particles in standpipe 231 in a fluid state. The partially spent catalyst particles enter the lower portion of riser 234 from standpipe 231 where they are combined with a fluidizing gas, such as steam, which enters the lower portion of riser 234 by means of line 235. The partially spent catalyst particles are carried upwards through

riser 234 and are discharged into the upper portion of second contacting zone 230 of vessel 210 above top tray 236. Horizontally arranged perforated plates or trays 236, 237, and 238 are provided in contacting zone 230 to provide intimate contacting between the hydrocarbon vapors and the partially spent catalyst. The catalyst in zone 230 is maintained in separate dense fluidized beds on plates 236, 237 and 238.

The rising hydrocarbon vapors pass through the opening in the plates and then flow through the dense fluidized bed on each plate. Each perforated plate is provided with a downcomer which maintains a definite level of catalyst on each plate and also provides a means for the catalyst to flow from one tray to the tray below. The top of the downcomer of trays 237 and 238 is installed at a sufficient height above each tray so as to maintain the level of the fluidized bed of catalyst on each tray above the bottom of the downcomer from the tray above in order to prevent the hydrocarbon vapors from passing up through the downcomer to the tray above. In Figure 3, partially spent catalyst discharged from riser 234 forms a dense turbulent fluidized bed on top of plate 236. As additional catalyst is discharged from riser 234, a portion of the catalyst on plate 236 flows into downcomer 239 and passes to plate 237 where it flows to the left in Figure 3 across plate 237. The catalyst then flows into downcomer 240, passes to plate 238, flows across plate 238 to the right in Figure 3, and passes into downcomer 241. Downcomer 241 differs from the other downcomers in that the catalyst from downcomer 241 is discharged into separating zone 217. Downcomer 241 communicates with separating zone 217 by means of an opening in annular plate 218. Catalyst leaving downcomer 241 is thus introduced to separating zone 217 at the wall of vessel 210 where the catalyst combines with the catalyst being separated in separating zone 217 and then moves downward due to the force of gravity into the dense fluidized bed in stripping zone 219.

This modification of the invention is not restricted to three such plates as shown in Figure 3 since one or more plates can be employed for the purposes of the present invention. Also, any equivalent contacting means could be employed in contacting zone 230. Also, the partially spent catalyst withdrawn from contacting zone 230 could be passed directly to rise 223 or to regenerator 211 after separately stripping any entrained hydrocarbons from it. It is preferable to employ spent catalyst in contacting zone 230 because the purpose of the catalytic aftertreating step in contacting zone 230 is to provide a mild cracking step with little coke formation so as to convert the diolefins which were formed in the thermal cracking step in soaking zone 229 to saturated hydrocarbon forms. This step improves the

octane number of the gasoline fraction and, in addition, improves the stability of all the hydrocarbon products from the process including the gasoline and middle distillate fractions. Also, a minor amount of additional conversion, namely, 2—6%, is effected in the catalytic aftertreating step.

The hydrocarbon vapors, or resultant stable lower boiling components from the original hydrocarbon gas oil, rise from contacting zone 230 together with a minor amount of entrained catalyst particles and pass through cyclone separator 242 wherein the vaporous hydrocarbon products are separated from the entrained catalyst. The hydrocarbon vapors essentially free from catalyst leave the top of vessel 210 by means of conduit 243 and the catalyst particles separated from the hydrocarbon vapors in separator 242 are returned to the dense fluid bed on plate 236 in contacting zone 230 by means of dip leg 244.

Other forms of apparatus useful for the process will be suggested by studying Figure 3. For example, it is not necessary that the soaking step and catalytic after-treating step be effected in one vessel, as shown in Figure 3, since two separate vessels may be employed to effect the same results. Also, by way of example, it is possible to perform substantially all of the initial catalytic cracking step in the same vessel as is utilized for the thermal cracking and catalytic aftertreating steps, rather than in a separate transfer line reactor as shown in Figure 3. One vessel or a number of separate vessels can be used for the process of the present invention.

Also, it is possible to employ freshly regenerated catalyst in the catalytic aftertreating step, but as has been previously stated, it is preferable to employ a partially spent catalyst so as to minimize coke formation on the catalyst employed in the catalytic aftertreating step. Although the present invention is especially advantageous for converting gas oils which produce a high proportion of coke to gasoline, such as gas oils having a high aromatic or nitrogen content, the present invention may be advantageously utilized with any type of hydrocarbon cracking feed stock.

The following example of the modified form of the process is not intended to limit the present invention but rather to illustrate the operation of the present process and its advantages over conventional catalytic cracking processes. In this example, 1000 liquid barrels/hour of hydrocarbon gas oil are preheated to a temperature of 600° F. and then are introduced into reactor 212. The gas oil has a boiling range of 600 to 1050° F., and is from a Los Angeles Basin crude oil. At the same time, 1800 tons/hour of synthetic silica-alumina catalyst, having a size range of 10 to 100 microns, at a temperature of 1100° F. are also introduced into reactor 212 from regenerator 211 so that the temperature of the resultant

catalyst-oil mixture is 980° F. Under these conditions, the catalyst/oil ratio on a weight basis is approximately 11 to 1 in reactor 212. Reactor 212 is 6 feet in diameter and 50 feet long. The space velocity of the hydrocarbon vapors in reactor 212 is 40 w/w/hour and the superficial velocity of the hydrocarbon vapors in reactor 212 is 15 ft./sec. The pressure in reactor 212 is 20 psig. Under the above cracking conditions, the conversion of the hydrocarbon gas oil to gasoline, other low boiling components and coke is 40% by volume with 5.0% by weight of the hydrocarbon gas oil converted to coke. Approximately 8 tons/hour of coke are thus formed on the catalyst in reactor 212.

The partially converted hydrocarbons and partially spent catalyst from reactor 212 are discharged into separating zone 217 at a temperature of 960° F. and a pressure of 17 psig. The superficial velocity of the hydrocarbon vapors in separating zone 217 is 1 ft./sec., and their residence time in separating zone 217 is 10 seconds. The hydrocarbon vapors pass upward from separating zone 217 into soaking zone 229 wherein the average temperature of the hydrocarbon vapors is 950° F. and the pressure 15 psig. The residence time of the hydrocarbon vapors in soaking zone 229 is 30 seconds and the superficial velocity of the hydrocarbon vapors again is 1 ft./sec. An additional 10% by volume of the hydrocarbon vapors is converted to gasoline and other lower boiling components, with about 4.0% of the total hydrocarbon vapors from soaking zone 229 being diolefins.

Approximately 1600 tons/hour of catalyst, on a coke free basis, are withdrawn from standpipe 222 and are combined with 65 MCF/minute of air in riser 223. In the regeneration step, 10.5 ton/hour of coke are burned off the catalyst in riser 223 and regenerator 211 at a temperature of 1100° F.

At the same time, 200 tons/hour of catalyst, on a coke free basis, are withdrawn from standpipe 222 by means of standpipe 231 and are combined in riser 234 with 7000 lbs./hour of steam from conduit 235. The 200 tons/hour of partially spent catalyst are discharged from riser 234 onto top plate 236 of a series of plates 236, 237 and 238 of contacting zone 230 on each of which plates a fluid bed of catalyst 8 inches in height is maintained. The temperature in contacting zone 230 is 950° F. and the pressure in the zone is 14 psig. Approximately 2.5 tons/hour of coke are formed on the catalyst in contacting zone 230, and an additional conversion of 4% is effected in this zone. From contacting zone 230, about 200 tons/hour of catalyst on a coke free basis are withdrawn by means of downcomer 241 and are passed to separating zone 217. Hydrocarbon products are withdrawn from the upper part of vessel 210 through conduit 243 and less than 1.0% of the total hydrocarbon products are

undesirable diolefins. The gasoline fraction of the final hydrocarbon products has an octane number (F-1) of 95 and the total conversion effected in this example of the present invention is 54%.

In a conventional catalytic cracking process to obtain the same percentage conversion with the particular type of gas oil and type of catalyst employed in the above example, and when employing the same hydrocarbon gas oil feed rate as above, 16.5 tons/hour of coke would be formed on the catalyst. The gasoline fraction from the conventional catalytic cracking process would have an octane number (F-1) of 95, being therefore no higher than in the process of the present invention, and the diolefin content of the total hydrocarbon products would be 1.0%.

Thus, the overall liquid product quality and yields from a conventional catalytic cracking process and the modified process of the present invention are equivalent for all practical purposes in this comparison. However, a conventional catalytic cracking process will produce 55% more coke for the same percentage of conversion and would therefore require 55% more regeneration capacity to burn the coke off of the catalyst. Another way of looking at the advantages of the present process is that, in a conventional catalytic cracking system, if catalyst regeneration facilities are limited to burning 10.5 tons of coke/hour, the conversion of hydrocarbons to gasoline, other low boiling components and coke will be limited to about 44% conversion as compared to 54% conversion in the process of the invention.

What we claim is:—

1. A process for cracking a gas oil which comprises maintaining the oil in contact with freshly regenerated catalyst in a conversion zone at from 850—1000° F. until there is produced a vaporous hydrocarbon product containing a substantial amount of hydrocarbon components boiling below 430° F. together with coke, not more than 5% by weight of the gas oil being converted to coke, passing the product substantially free of catalyst into a soaking zone where it is heated to a temperature in the range of about 850° to 1150° F. to produce additional hydrocarbon components boiling below 430° F. but substantially no coke.

2. A process as claimed in Claim 1, in which the product is maintained in the soaking zone for a period sufficient to convert 5—20 vol. % of the original gas oil to products boiling below 430° F.

3. A process as claimed in Claim 1, in which the product is maintained in the soaking zone for from 0.5 to 10 seconds at a temperature maintained at about 1050—1150° F.

4. A process as claimed in Claim 1, in which the product is maintained in the soaking zone for from 0.5 to 5 minutes at a temperature maintained at about 850—1050° F.

5. A process as claimed in Claim 3, in which the temperature of the soaking zone is maintained at about 1075—1125° F.

6. A process as claimed in Claim 4, in which the temperature of the soaking zone is maintained at 900—1000° F.

7. A process as claimed in Claim 1, 2, 4 or 6, in which the products from the soaking zone are subjected to further catalytic treatment whereby at least a major proportion of any diolefins present are converted to saturated hydrocarbons.

8. A process as claimed in Claim 7, in which the catalyst used in the further catalytic treatment is spent catalyst from the conversion zone.

9. A process as claimed in any one of the preceding claims, in which the gas oil is maintained in the conversion zone for a time sufficient to convert 30—50 vol. % of it to coke and hydrocarbons boiling below 430° F.

10. A process as claimed in any one of Claims 1—8 in which the gas oil is passed through a fluidized bed of catalyst in the conversion zone at a superficial velocity of from 1 to 3 ft./sec.

11. A process as claimed in any one of the preceding claims, in which the gas oil is mixed with a hot finely divided catalyst and passed through the conversion zone at a superficial velocity of from 6 to 15 ft./sec.

12. A process for cracking hydrocarbon oils substantially as described and illustrated with reference to any one of the figures of the accompanying drawings.

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Agents for the Applicants.

Fig. 1.

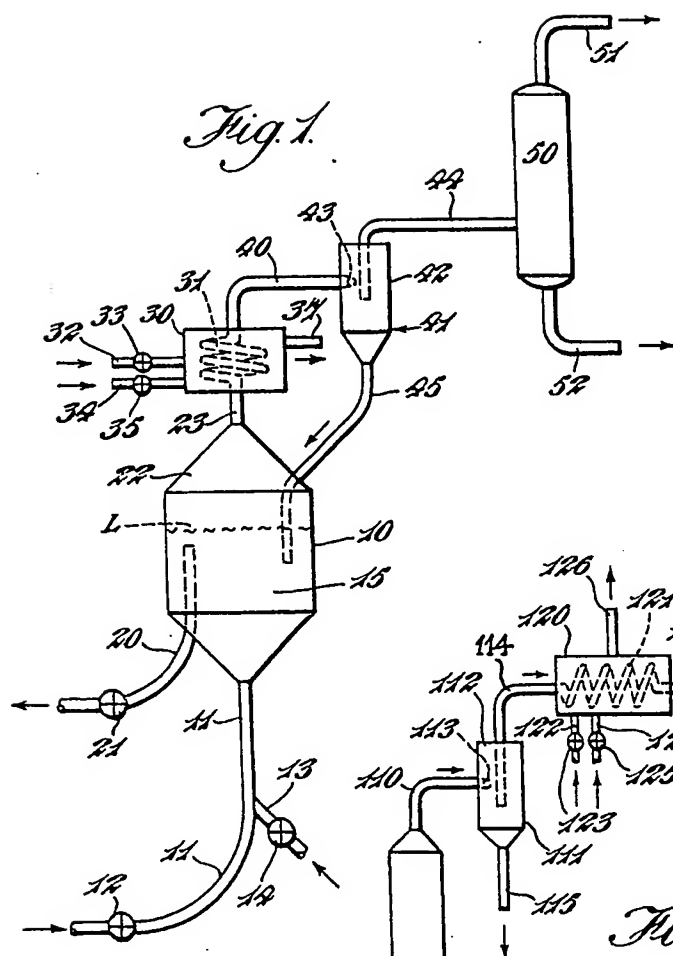


Fig. 2.

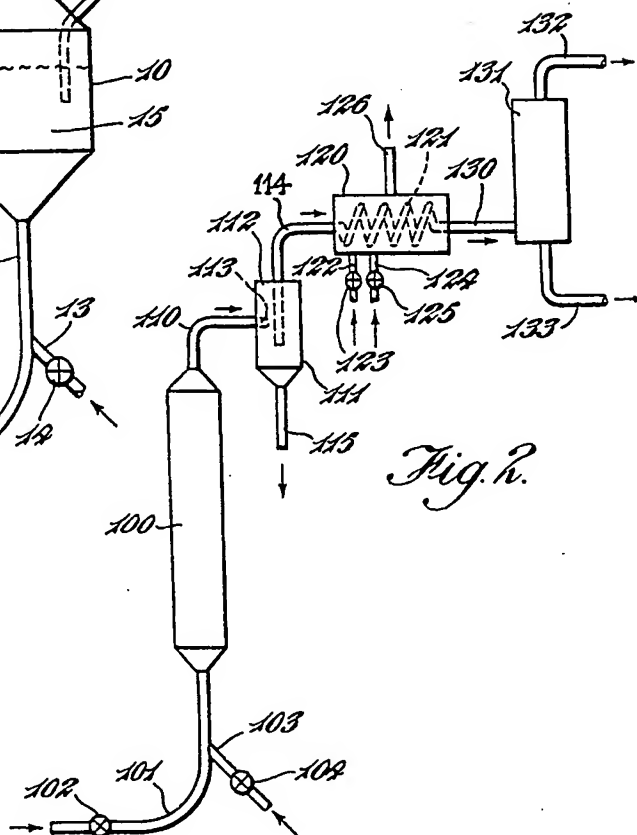
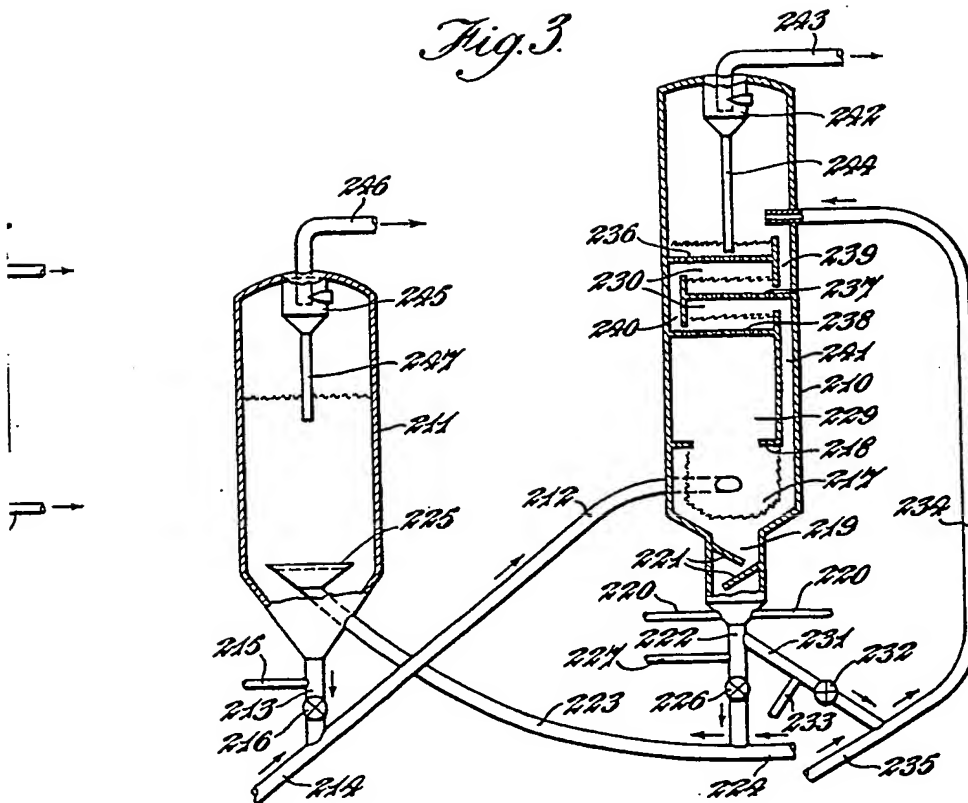


Fig. 3.



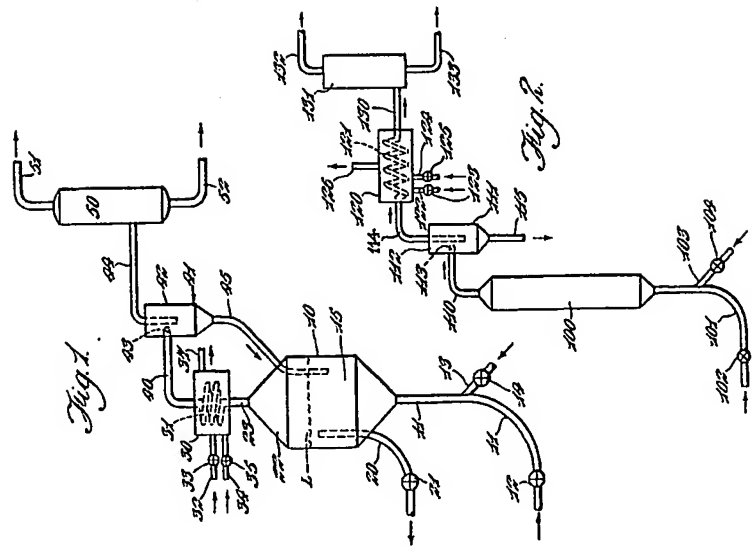


Fig. 1.

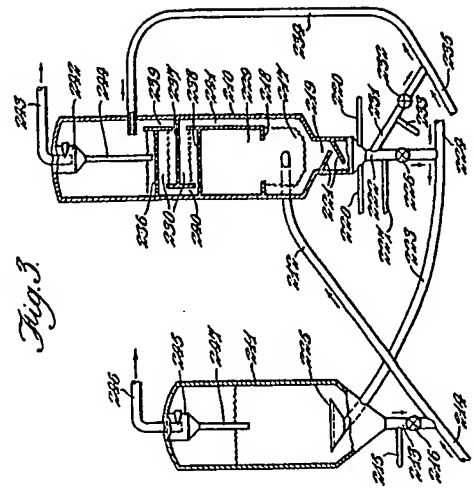


Fig. 2.

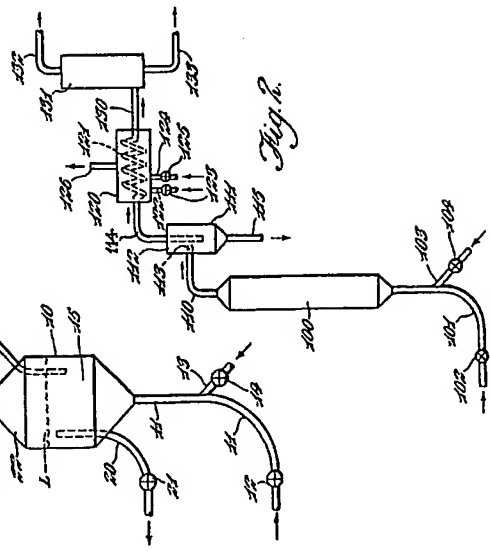


Fig. 3.